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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

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G. W. FOX

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THE EXCITATION OF THE SPECTRA OF CARBON MONOXIDE BY ELECTRONIC IMPACTS

BY G. W. FOX

ABSTRACT

The *ionization potential* of the carbon-monoxide molecule was *determined* with the *low-voltage arc* to be 14.3 volts.

The band spectra of carbon monoxide were excited in tubes with two and three electrodes, and the *excitation potentials* for the various systems were *determined* by the photographic method. *Two parallel sets of levels* occur for the *neutral* molecule with values 6.0, 10.34, 11.35 volts for one set and 8.0 and 10.73 volts for the other set. The systems have been correlated to transitions between these levels.

The third positive carbon bands reported by Deslandres have been shown to be due to carbon monoxide.

Complete analysis of the *third* positive system has been made, and a new system proposed.

The *ionized* carbon-monoxide molecule was found to have *three levels* with values 16.9, 20.0, and 22.9 volts. The systems of *negative bands* have been correlated to *transitions* between these levels.

This paper deals with the critical potentials and spectra of carbon monoxide. It is companion to papers by O. S. Duffendack,¹ D. C. Duncan,² and L. L. Lockrow³ in which have been described researches on hydrogen, nitrogen, and oxygen. The work is divided into three parts. The first deals with the electrical behavior of the gas under various conditions of electronic excitation and pressure, and from these data the ionization potential is determined. The second part deals with the determination of the critical voltages necessary to excite the band spectra of neutral and ionized carbon monoxide. The last part deals with the origin of the "carbon-oxide" bands. (In the last two parts of the work the spectroscope was used.)

PART I. THE ARC

The low-voltage arc provides an ideal means for the production of the spectra of gases, and also furnishes a very easily controlled arrangement for examining their electrical characteristics. This method of excitation was used throughout the entire work. The

¹ *Physical Review*, 20, 665, 1922.

² *Astrophysical Journal*, 62, 145, 1925.

³ *Ibid.*, 63, 205, 1926.

theory of the low-voltage arc as developed by Duffendack¹ and by K. T. Compton² leads to the conclusion that the sudden large increase in current results from a neutralization of the negative space-charge surrounding the filament. At low voltages, i.e., at low electronic velocities, the region immediately surrounding the filament will be at about the potential of the filament, provided the temperature of the filament is high enough to insure a copious emission. The current is limited by the space-charge. At higher voltages some ionization may set in due to the increased energy of the electrons at collision. The positive ions formed neutralize the negative space-charge surrounding the filament; and, since each ion can neutralize the space-charge of a large number of electrons, a large increase in electronic emission results; this is termed "striking the arc." Under this condition practically the entire fall of potential across the tube occurs in the immediate vicinity of the cathode. As a result there is increased ionization near the cathode, with the consequent formation of more positive ions which still more fully neutralize the space-charge of the electrons. The result is a value of the current which closely approximates that given by O. W. Richardson's equation.³

APPARATUS

The discharge tube was made of pyrex glass of the form shown in Figure 1. Each end was closed by a ground-joint stopper, one of which carried the filament leads of tungsten, and the other the lead to the anode and a second electrode which supported a grid in a later part of the investigation. On one side of the tube was a quartz window through which the radiation could be photographed. From the top of the tube a glass connection led to the liquid-air trap and then to the pumping system. The ground joints of the stoppers and window were sealed with hard De Khotinsky cement, water cooled, and no stopcock grease was used. The tube and electrodes were completely outgassed before CO was admitted.

A tungsten anode and filaments in the form of a five-turn helix of 12-mil tungsten wire were used throughout most of the work, the filaments being spot-welded to the supports. The anode was made

¹ *Physical Review*, **20**, 665, 1922.

² *Ibid.*, **21**, 266, 1923.

³ *Emission of Electricity from Hot Bodies*. 2nd ed. p. 35.

in the form of a square U turned on its side. Both filament and anode were so arranged as to lie on the axis of the tube, the distance from the filament to any part of the anode being about 6 mm. By this arrangement the characteristic "sky-blue" glow of carbon monoxide could be well concentrated between the electrodes. A single-stage mercury pump backed by a Cenco Hyvac pump made up the vacuum system. Pressures were read on a McLeod gauge.

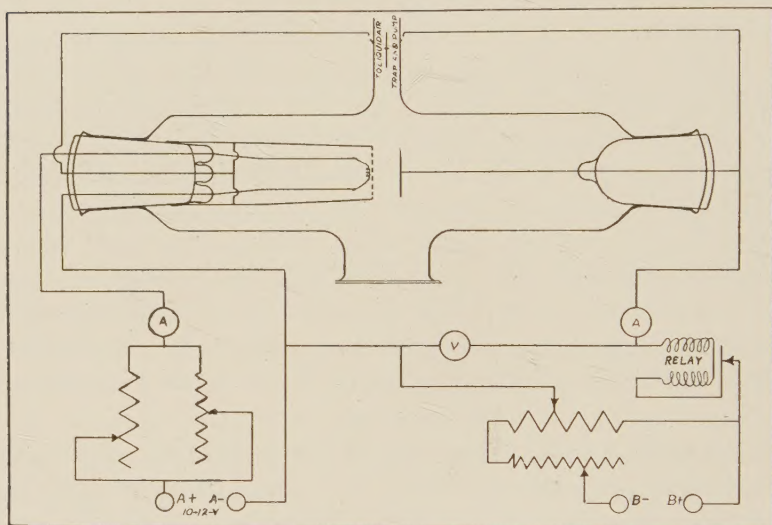


FIG. 1.—Discharge tube and circuit arrangement

The carbon-monoxide gas was generated outside the system entirely. Especially prepared oxalic-acid crystals were heated in the presence of concentrated sulphuric acid. Carbon monoxide containing a trace of carbon dioxide is produced by this method. The two gases, together with any water-vapor not removed by the acid, were then passed through a wash bottle containing a concentrated solution of potassium hydroxide to remove the CO_2 . The remaining gas was then passed through a drying-tube containing phosphorus pentoxide to remove still further any moisture, and then into an evacuated flask, which was allowed to fill up to atmospheric pressure. This flask of gas was then sealed to the vacuum system and isolated from the discharge tube. Since in this type of work the gas

pressure never exceeds a few mm at most, two bottles of gas were found to more than suffice for the entire investigation.

The circuit employed was the usual low-voltage arc circuit. The plate current was read on a Paul unipivot milliammeter. The plate voltmeter was connected from the plate of the tube to the negative side of the filament. Since the middle turn of the filament is the hottest and therefore the most efficient in electronic emission, one-half the voltage drop along the filament has been, in all cases, subtracted from the voltmeter reading, and this corrected value is called the true difference of potential between the electrodes. Further discussion of this correction will be made later.

DETERMINATION OF THE ARCING POTENTIAL

To determine the effect of pressure changes on the arc, a series of runs were made at constant filament voltage and various pressures. In all cases the potential of the "break" was somewhat lower than that of the "strike" and is believed to be more characteristic of the ionizing potential.¹ It is this voltage from which the ionizing potential was determined. As it is a well-known fact, borne out by repeated observation, that an arc cannot be maintained in a diatomic gas at a voltage less than the ionization potential, this procedure seems justifiable. At low pressures the value of the mean free path between effective collisions is large compared to the interelectrode distance. Little ionization occurs until the part of the path in which ionizing collisions can occur is a large fraction of the total path. At the optimum pressure the electrons make the largest number of ionizing collisions while traveling from cathode to anode. Above this pressure, electronic energy is lost by impacts and momentum exchanges with gas molecules. Over the range from 0.4 mm to 1 mm no particular difference could be noted in the breaking-potential of the arc. Above or below this range, however, the breaking-potential increased markedly. The lowest voltage at which the arc could be maintained in carbon monoxide was 14.3 volts, which value represents the ionization potential of the molecule, in agreement with the values obtained by other methods.² Knowing this

¹ Duffendack, *op. cit.*

² *Bulletin of the National Research Council on Critical Potentials*, No. 48, p. 120.

value, it can be said with certainty which of the emitted radiations are due to the neutral, and which are due to the ionized, molecule. This at once divides the field of investigation into two parts which will be dealt with in detail later.

There were no oscillations observed in carbon-monoxide arcs. A cathode-ray oscillograph was connected across the discharge tube, and typical runs were made in exactly the same manner as when determining the ionizing potential. No fluctuation in the cathode beam across the field could be detected except the slight fall or rise of the beam corresponding to the slight voltage drop or rise indicated also by the voltmeter when the arc struck or broke.

PART II. THE CARBON-MONOXIDE SPECTRA

Few gases possess so diversified a band spectrum as carbon monoxide. From well out in the red its band systems extend through the visible and ultra-violet regions apparently as far as one chooses to penetrate. In this part of the work the object has been to isolate these different spectra, so far as possible, and to determine the critical amounts of energy necessary to excite them. In this way one can assign each particular system to its proper origin and establish some physical relations between systems. With this object in view, therefore, a spectrographic study was made of the radiations emitted by the carbon-monoxide molecule when excited by electrons of known velocities.

Above the ionization potential, low-voltage discharges were maintained in carbon monoxide contained in the simple two-element tube previously mentioned. For investigation below the ionization potential, this tube was modified by the introduction of a third electrode: a grid made of a cylinder of thin nickel having a small platinum gauze window in the end. This cylinder fitted over the filament supports and was mounted so that the distance from filament to gauze window was less than one millimeter. The plate and grid were then electrically connected, and radiation from the force-free region was photographed through the quartz window in the side of the tube (Fig. 1).

Observations obtained above the ionization potential with this arrangement and with the two electrode tubes were in very good

agreement. This is to be expected according to the theory of the low-voltage arc, for when the arc strikes, a redistribution of potential takes place in the tube, so that almost the entire voltage drop occurs very close to the cathode. We should expect, therefore, that on the first collision the electrons should have a velocity practically equal to the applied potential difference.

The critical potentials for each system were determined by photographing throughout a certain voltage range, first using voltage-intervals, and then, in cases where greater accuracy could be had, by using intervals as small as 0.1 volt. For systems which are not superposed, accuracy as great as 0.2 volt is entirely possible. If conditions could be arranged to allow the appearance of a single system at a time, accuracy as high as 0.2 volt should be the rule. Unfortunately, in those systems above the ionizing-potential, one system may come in after several others in the same region are developed; and it is difficult, in such cases, to locate the excitation potential closer than half a volt.

The values of the critical potentials listed in Table I are *corrected* values. The potential difference was in all cases applied between the plate and the negative end of the filament. As this voltage is increased, the potential difference between the anode and the negative end of the filament reaches the critical value first. Consequently, the few electrons emitted by this portion of the filament attain velocities of such magnitude that on long exposure a faint spectrogram of the band system—or at least, of the bands originating in the lower vibrational levels—can be developed. As the applied voltage is increased, a point is reached at which the potential difference between the central turns of the helical filament and the plate reaches the critical value. The central turns of the filament are the hottest and furnish nearly all the electronic emission. At this point the band system suddenly develops. A further slight increase in the applied voltage brings the potential difference between the last portion of the filament and the anode up to the critical value. This will slightly increase the number of critical-speed electrons, but the percentage increase is so small that no effect on the intensity of the band systems can be detected. The values of the critical potentials are, therefore, the values of the voltage between the anode

and the middle of the heated cathode after the band system has developed. This means that half the IR drop along the filament has been in each case subtracted from the actual voltmeter reading.

The situation is shown graphically in Figure 2, which is based on a calculation from a typical 5-turn tungsten filament as used throughout this work. The information regarding tungsten emission used in sketching the curve was taken from data furnished by the General Electric Company and the Nela Research Laboratory. Some allowance was made for possible heating of adjacent turns due to radiation, but in a personal letter Dr. Dushman says this effect

TABLE I
CRITICAL POTENTIALS

Band System	Direction of Shading	Excitation Potential Observed (Volts)
Ångström (second positive).....	Toward violet	10.7
Deslandres (fourth positive).....	Toward red (beyond range of investigator)	8.0 (calc.)
Cameron.....	Toward red (not observed)	6.0 (calc.)
Third positive.....	Toward violet	10.2
3 A (positive).....	Toward violet	11.1
Deslandres (first negative).....	Toward red	20.0
"Comet-tail" (third negative)....	Toward red	16.9
Baldet-Johnson.....	Toward violet	22.9

is small for filaments of the type used. This points at once to the middle turn as the source of most of the electronic emission.

To test the validity of the correction, determinations were made of the critical potential of a certain system using both the tungsten filaments and filaments of oxide-coated platinum. In these two cases the voltage drops along the filaments were widely different: for the tungsten, about 2.5 volts, and for the oxide filaments, 0.8 volts. The correction for initial velocity of electrons should also be very different since the oxide filament was run at a very dull-red heat and the tungsten at a white heat. Further, there are different contact electromotive forces to consider. However, determinations of the excitation potential in the two cases, applying the same correction, i.e., one-half the voltage drop along the filament, gave values of the critical potential only 0.1 volt apart. Since determina-

tions of the critical potentials with two different types of filaments agree within 0.1 volt, when the same correction is applied in each case it would seem that this method of correction is legitimate.

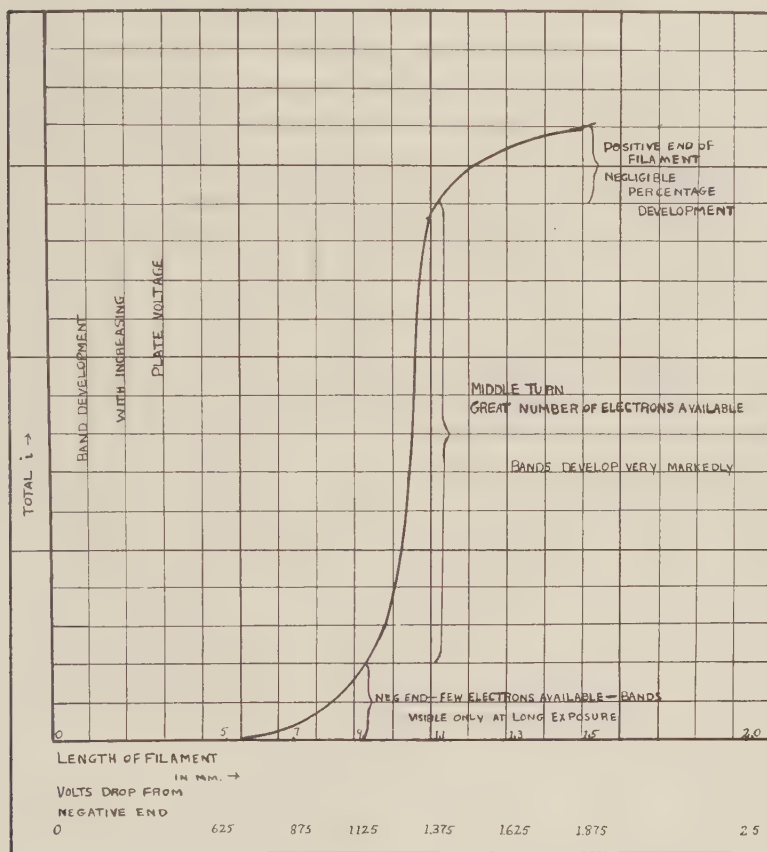


FIG. 2.—Curve showing band development with increasing voltage

To further test this point, a 3-turn tungsten spiral was used to check the determined excitation potential of one system. The voltage drop over this filament was less than over the 5-turn spiral, and emission is almost wholly from the middle turn. Again the same method of correction led to agreement in results. It may be said, furthermore, that the corrections applied in all cases were such as

to make the excitation potential of the Ångström system 10.7 volts. The excitation potential of this system can be computed with certainty because of its relation to the fourth positive system which has been obtained in absorption.

RESULTS

The carbon-monoxide band spectrum comprises three negative systems commonly known as the "first negative," "third negative" or "comet-tail" bands, and the "Baldet-Johnson" bands. The positive systems are known as the "second positive" or "Ångström" bands, the "Cameron" bands, the "third positive" bands, and a system to be designated as the "3 A" bands. These systems, together with their directions of shading and corresponding observed excitation potentials, are given in Table I.

The Ångström bands.—In an old work¹ published in 1875, Ångström and Thalén gave the measurements of the heads of this band system which has ever since borne Ångström's name. These bands begin at 6622 Å and extend intermittently throughout the entire visible spectrum. They do not occur in groups, but as single bands having a very decided edge and shading off markedly toward the violet.

This system was not excited until the P.D. between the anode and middle of the filament reached 10.2 volts. By long exposure at this voltage, the edges at 4511 Å and 4834 Å could be seen very faintly. Increasing the voltage in 0.1-volt steps brought out a decided development of the system at 10.7 volts, above which value no great development occurred. Consequently the excitation potential was fixed at 10.7 volts in accordance with the expected development of the bands with increasing voltage as outlined above. The same procedure was followed for each band system. It is interesting to note that although this system comes in well below the ionizing-potential it is exceedingly strong no matter what voltage is applied above its exciting potential. At 200 volts these bands are remarkably brilliant, their fine structure being especially well developed.

The Ångström bands are best produced in the low-voltage arc

¹ *Nova Acta Regiae Societatis Scientiarum Upsaliensis*, 9, 1875.

at pressures of the order of a millimeter. At low pressures of 0.01 mm, or less, nothing but the edges remain, and even these are faint. This is a high-pressure system.

Table II gives the wave-lengths and wave-numbers of these bands. They are shown in two groups, "A" and "B," as previously classified.

TABLE II
Ångström Bands

Previously Reported λ	By Writer λ	$1/\lambda$	Intensity
Group A			
4209.0	Not observed	23759	
4511.0	4512.1	22156	10
4834.0	4834.8	20678	9
5197.0	5197.6	19235	10
5607.5	5609.8	17821	10
6078.0	6080.2	16442	8
6622.0	6619.9	15102	5
Group B			
4131.0	4126.4	24227	7
4394.0	4392.2	22756	8
4697.0	Not observed		
5015.0	Not observed		
5397.5	Not observed		
5817.0	Not observed		
New Bands			
	4380.1	22824	7
	3894.8	25667	6
	3679.5	27170	9

As will be noticed, only part of the bands originally recorded as belonging to this system have been observed during this investigation. The bands at 4380.1 Å, 3894.8 Å, and 3679.5 Å have not been reported previously. These bands are very strong on all plates of the Ångström system; and, although they do not fit into the scheme proposed by Raymond T. Birge,¹ their appearance and behavior indicate that they should be included in the system. His arrange-

¹ *Nature*, 117, 230, 1926.

ment of the so-called "B" group¹ does not fit the given wave-lengths very well. Neither do the newly observed bands fit into this arrangement. Indeed it seems doubtful if his analysis is a legitimate one, since the existence of so many of the reported edges is questionable. The bands at 4380 Å and 4394 Å show curious intensity relations with the voltage. At low voltages of the order of 15 volts, 4393 Å is very much the stronger; while at higher voltages, of around 100, 4394 Å practically disappears and 4380 Å is very strong. Further analysis will be necessary to straighten out this matter over which there has been some controversy.^{2,3} Later, a suggestion will be offered to account for the bands not observed in this investigation. Plate VI shows the development of the Ångström system through the critical voltage range.

Fourth positive system.—This system originally classified by Deslandres is another familiar one commonly attributed to carbon. It usually appears in Geissler-tube discharges where the tubes have been sealed with stopcock grease. There are in all about 150 bands in this system, extending from about 2500 Å down to about 1500 Å. It was impossible to photograph any of the bands of this system below 10.5 volts. Recently, Sigmund W. Leifson, in working with absorption spectra in the extreme ultra-violet,⁴ has photographed some bands which Birge⁵ has identified as the 0-0, 0-1, 0-2, . . . 0-11 transitions of this system. These bands lie well below the region in which the quartz spectrograph is effective, and this explains why only the bands of the higher vibrational levels could be photographed. The computed value of the critical potential as determined from the absorption spectrum is 8.0 volts. All the bands lying between 2000 Å and the upper limit of the system have been identified. They are well developed above the ionizing-potential, though at higher voltages the overlapping by the first negative bands somewhat obscures them.

Cameron bands.—W. H. B. Cameron⁶ recently reported a new system of bands produced by Geissler-tube discharges in neon at

¹ Birge, *Physical Review*, 28, 1157, 1926.

² E. Hulthen, *Annalen der Physik*, 71, 41, 1923.

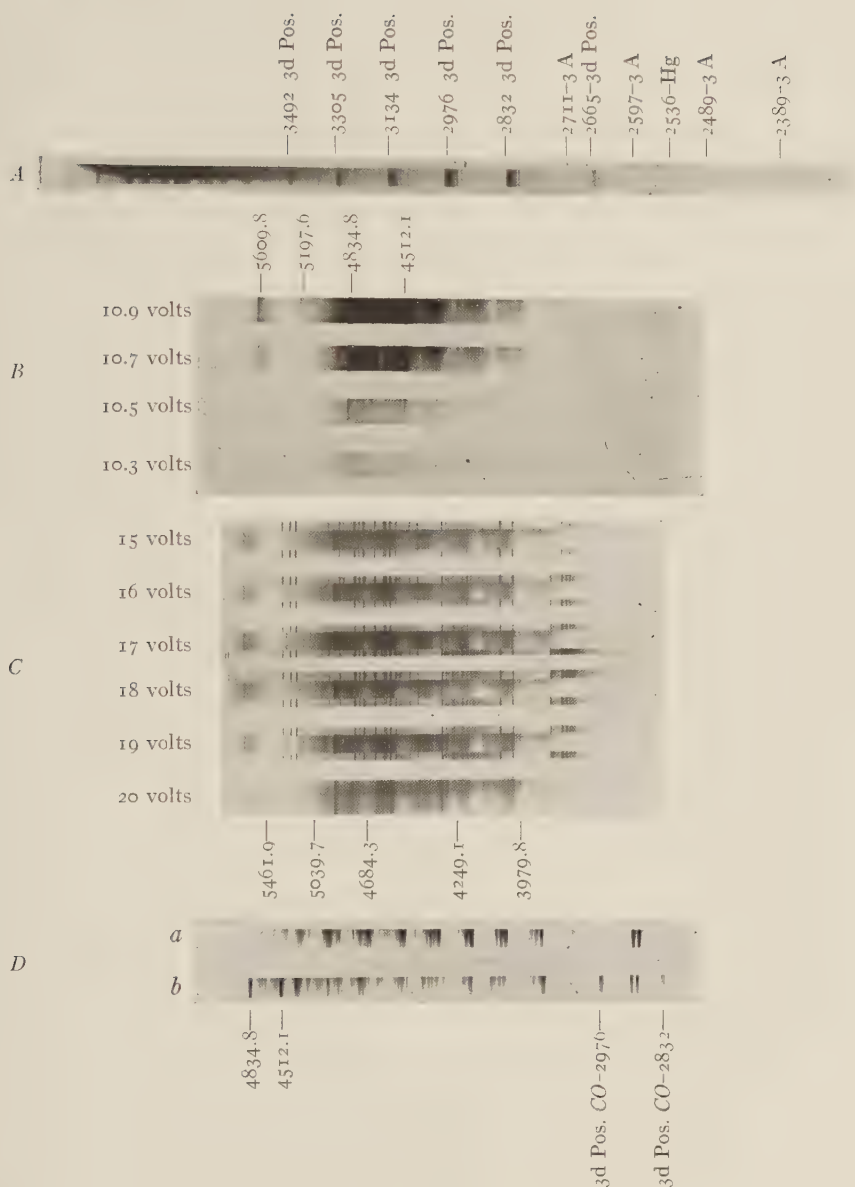
³ R. Mecke, *Physikalische Zeitschrift*, 26, 217, 1925

⁴ *Astrophysical Journal*, 63, 73, 1926.

⁵ *Nature*, *op. cit.*

⁶ *Philosophical Magazine*, 1, 405, 1926.

PLATE VI



A.—Bands of third positive system of CO and 3 A bands of CO
 B.—Showing development of Ångström Bands through Critical Range
 C.—Development of "Comet-Tail" Bands through Critical Voltage Range
 D.—a) CO₂ Flowing Gas
 b) CO₂ Stagnant Gas

high pressure when carbon electrodes were used. This system lies between 2100 Å and 2600 Å and falls into three or four groups having five heads each. All these groups are very weak, and careful examination of a large number of plates of this region does not show them definitely present. Attempts to excite this particular system are unsuccessful, largely because of the far greater excitation of the first negative and fourth positive systems which lie in the same region. R. C. Johnson¹ definitely attributes this system to carbon monoxide and computes 6 volts as the exciting potential.

Third positive bands.—Extending from just below the visible down to about 2250 Å are bands which, since their original measurement by Deslandres, have been called the “third positive carbon bands.” On examination of these bands, one notices two types of structure quite dissimilar in appearance. The bands which will be called the “third positive carbon bands proper” are very complex, each band being made up of as many as five or six heavy subheads which cause them to appear as blurred and indistinct groups. Because of this complicated structure, the third positive system has been generally attributed to carbon dioxide, though no definite attempts have been made previously to determine its origin. The critical potential as observed was 10.2 volts.

In examining the development of this system, it was noted that part of it came in at almost a volt higher potential than that just given. Closer examination revealed that these latter bands, though classed with the third positive, were in reality quite different. Whereas the previously described bands were made up of as many as six heads to the group, very complicated in appearance, these consisted of only double-headed groups. Though both types were shaded toward the violet, examination showed a striking difference in the appearance of their fine structure. The bands of the double-headed nature, which will be designated as the “3 Å system of carbon monoxide,” have very sharp edges. Their fine structure at the higher voltages is exceedingly well defined and quite widely spaced. In general, the intensity of the 3 Å system is less than that of the third positive system. Though both come in well below the ionization potential, they persist strongly at voltages above it.

The effect of reduced pressure is very noticeable on all these

¹ *Nature*, 117, 377, 1926.

bands. At about 1 mm both systems are well developed at 13 volts exciting-potential. As the pressure is diminished, the intensity decreases markedly, until at very low pressure, when it is difficult to maintain the discharge, these systems can be photographed only with the longest exposures. This is in accord with F. Baldet's observation.¹

Table III gives the bands which properly belong to the third positive system, together with those bands which have been named the "3 A system of carbon monoxide."

TABLE III
THIRD POSITIVE AND 3 A BANDS

Third Positive		3 A Carbon Monoxide	
λ	τ/λ	λ	τ/λ
2832.0	35311	2295.2	43569
2976.4	33598	2389.0	41858
3134.6	31902	2489.9	40162
3305.3	30254	2597.1	38504
3492.7	28631	2711.35	36882
3698.7	27037		
2665.5	37521		
2792.7	35805		
3079.9	32469		
3241.8	30847		
3418.2	29253		
3612.7	27680		
3825.1	26143		

In connection with the negative band systems, i.e., those due to the ionized molecule, it may be well to call attention to the effects of cumulative ionization. During the course of the work, it was found that no consistent critical potential values could be obtained from arcs maintained in the two electrode tubes unless the arc current was kept small. This effect came up first in connection with the first negative system. The higher the arc current the lower the apparent critical potential of the system became. Indeed, it was perfectly possible to excite the first negative system very strongly at the ionizing-potential with arc currents of the order of 100 milliamperes. The reason for this is that when the positive-ion concen-

¹ *Comptes Rendus*, 180, 1201, 1925.

tration becomes large in the region surrounding the filament, the probability of exciting an ion by a second electron impact must be considered. As the energy necessary for the excitation of the ion is less than that essential for ionization, the electrons accelerated by a voltage equivalent to the ionizing-potential possess adequate energy to excite ions previously formed. However, when the ion concentration is small (small arc current) the probability of such cumulative process becomes insignificant, and both excitation and ionization must result from a single collision. In this case the electron must possess an amount of energy equal to that necessary to ionize plus that required for excitation. As mentioned previously, determinations of critical potentials were made above the ionization potential both with and without grids, the results checking very well. In such cases cumulative ionization was eliminated by keeping the arc current small.

First negative bands.—This system was discovered and classified by H. Deslandres¹ in 1903. In 1924 Johnson² produced the entire spectrum reported by Deslandres and was able to add several new members, chiefly on the less refrangible side of each band group. Plates produced during the present investigation show all the bands ascribed to this system by Johnson. These bands resemble the nitrogen systems in general appearance. They are arranged in distinct groups and shade toward the red. The critical exciting potential of this system as observed was 20.0 volts. Up to 200 volts, this system stands out remarkably clear and well defined. Though best developed at pressures of 0.5 to 1 mm, the first negative bands are still clearly visible at low pressures where it is difficult to maintain the discharge.

Third negative bands—"comet tails."—In 1908 A. de la Pluvinel and Baldet³ discovered some new bands in the spectrum of the comet Morehouse which they were unable to ascribe to any of the known band systems. After the announcement of their discovery, A. Fowler⁴ was able to identify the "comet-tail" bands with some he had

¹ *Comptes Rendus*, **137**, 457, 1903.

² *Proceedings of the Royal Society*, Series A, **108**, 343, 1925.

³ *Astrophysical Journal*, **34**, 89, 1911.

⁴ *Monthly Notices of the Royal Astronomical Society*, **70**, 176, 1909.

produced using Geissler-tube discharges in carbon monoxide at very low pressure.

The "comet-tail" bands are very readily produced in the low-voltage arc. They extend from the red through most of the visible spectrum and are characterized as narrow double-headed bands degraded toward the red. They lie in a particularly complicated region which is already occupied by the Ångström bands so that, at ordinary pressures, unless the exciting voltage is quite high, their presence might be entirely unknown. By decreasing the pressure to about 0.05 mm, the intensity of the Ångström bands can be greatly reduced and then the third negative system can be very beautifully developed. This system showed decided development at 16.9 volts, which value has been designated as the critical potential. Below this value, only by prolonged exposure could these bands be noticed at all. At higher voltage, as with the other negative systems, the "comet tails" become very brilliant, their fine structure standing out in great detail. This is a typical low-pressure system. Recently T. R. Merton and Johnson¹ have been able to develop these bands in a mixture of helium and carbon monoxide. They have measured the heads of all the bands belonging to this system with great accuracy. All the bands reported by Merton and Johnson appear on plates produced during this investigation, with good agreement as to intensities.

Baldet-Johnson bands.—This group of bands is typically a high-pressure system. Whereas the "comet-tail" bands and the first negative bands can be photographed at extremely low pressures, these entirely disappear at pressures below 0.05 mm even at voltages of the order of 100 or more. They are developed best from 0.8 to 1 mm of pressure. Baldet² and Johnson³ independently discovered these bands, which are characterized as groups, having four heads each, of small wave-number separation, and degraded toward the violet. These bands were in no way visible under 22.9 volts, but at this voltage a decided development occurred, the quadruple heads of the groups standing out very clearly.

¹ *Proceedings of the Royal Society*, Series A, 103, 383, 1923.

² *Comptes Rendus*, 178, 1525, 1924.

³ *Proceedings of the Royal Society*, Series A, 108, 343, 1925.

SYSTEM RELATIONSHIPS

The carbon-monoxide band systems can be conveniently represented on an energy-level diagram. This scheme in general shows only the electronic transitions, but it should be borne in mind that to each electronic level belong several vibrational levels accompanied by many rotational levels.

In this scheme of levels the lowest, namely the 6 volts and 8 volts belonging respectively to the newly discovered Cameron bands and the fourth positive bands, are proposed by Johnson¹ and Birge.² It was impossible to determine these potentials experimentally due to the region in which these bands lie. Johnson concludes that the initial levels of the Cameron bands coincide with the final levels of the third positive bands of carbon and computes for their excitation potential 10.34 volts. The observed value is 10.2 volts, which is within the experimental error for this type of work. At 11.1 volts, the 3 A system of carbon monoxide develops. The analysis of this system leads to the conclusion that its final levels are also the initial levels of the Cameron bands. That this is a new system and not part of the third positive system is borne out by the fact that it takes an additional volt to develop it. This represents a jump of somewhat over 8000 wave-numbers, a value too large for a vibrational difference. Figure 3 shows in detail the analysis of the third positive and 3 A systems, both of which follow Deslandres progressions of the first type. The third positive system has initial vibrational states 0 and 1, with final states 0-7; and the 3 A system has only vibrational state 0, and the same final states as the companion system. It is to be noted that these systems follow the general rule observed in all band spectra, that as the excitation potential of a system approaches the ionizing-potential the number of vibrational levels diminishes. The ionization potential acts as an upper limit to the amount of energy the neutral molecule can have; and as it is approached, the probability of ionization exceeds the probability of further increase of energy in vibrational form. The fact that these two systems have entirely dissimilar appearances, so far as fine structure is concerned, is further evidence that they are two distinct band systems.

¹ *Nature*, 117, 377, 1926.

² *Ibid.*, p. 230.

As mentioned previously, the third positive system has very generally been attributed to CO_2 because it was believed that the

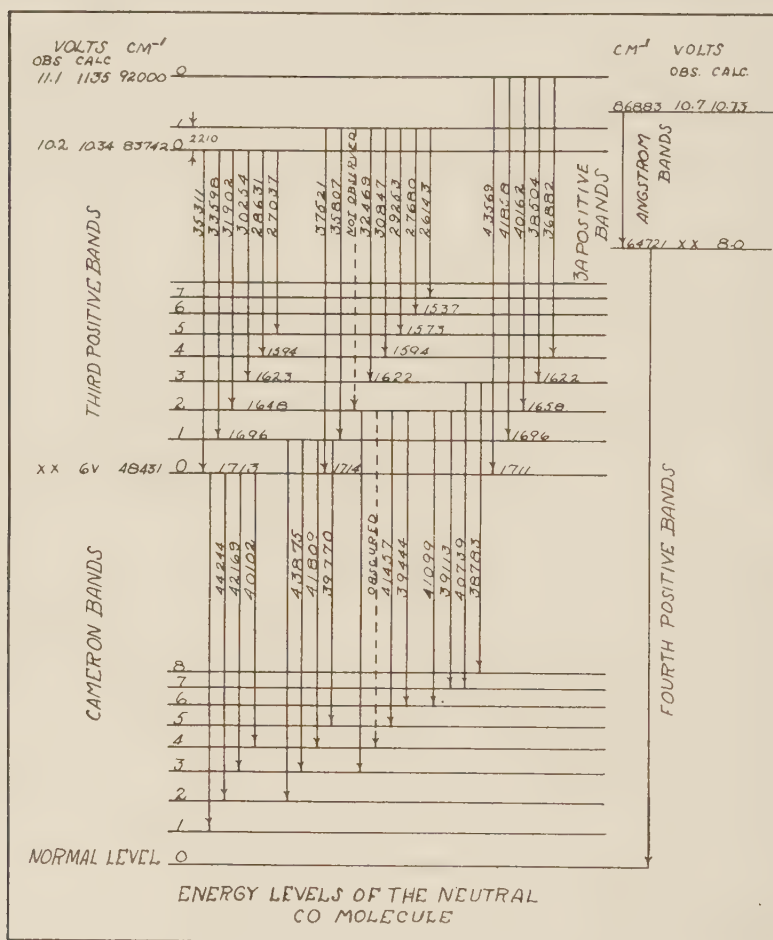


FIG. 3

bands were of too complex structure to belong to a simple diatomic molecule. However, the fine structure of these bands has never been analyzed and there is no direct evidence that they belong to CO_2 . Their relation to the Cameron bands points strongly to CO as their origin as suggested by Johnson.¹

¹ *Nature*, 117, 377, 1926.

The initial states of the Ångström bands lie between the initial states of the third positive and 3 A groups. On examination of these bands, one is at once struck with their pronounced simplicity as compared to the systems just described. Whereas both the third positive and 3 A bands are multiple headed, the Ångström bands possess very sharp single heads and degrade rapidly toward the violet. In their simplicity they resemble quite markedly the bands of the fourth positive system. Birge¹ has recently shown that the initial states of the fourth positive bands are identical with the final states of the Ångström system. His computed excitation potential almost exactly agrees with the value observed for this system. If 8 volts is accepted as the exciting-potential of the fourth positive system and if 4512 Å is the o-o band of the Ångström system, as Birge suggests, then the energy difference between the normal state of the neutral CO molecule and the initial state of the o-o band of the Ångström system would be 86,960 wave-numbers. According to the $h\nu$ relationship, this means the electronic energy associated with the o-o transition of the Ångström band system should be 10.73 volts. The observed critical potential for this system is 10.7 volts.

It will be noticed that the neutral CO molecule possesses two parallel series of electronic energy levels. This may very possibly mean that the CO molecule has two distinct types of spectral terms, corresponding to different types of electronic orbits. Whether or not combination band systems due to transitions between these two sets of levels are possible cannot be said. No such systems have been observed.

Considering along with R. S. Mulliken² the analogy between the band spectra just described and the spectra of the corresponding atom, a reasonable explanation can be proposed for the complexity of the third positive system. If each atom retains its own electrons in the K shell but shares those in the other shells, then the CO molecule would possess two valence electrons. Its molecular weight is 28. Hence according to the atomic analogy one would expect the spectra of the CO molecule to bear some similarity to the spectra of the magnesium atom, the spectral terms of which are singlets

¹ *Nature*, **117**, 230, 1926.

² *Physical Review*, **26**, 561, 1925.

and triplets. Pursuing this idea one is led to the possible conclusion that the complex structure of the third positive bands may be due to an overlapping from the several levels of the possible triplet terms. If the separations of the triplet levels are of the same order of magnitude as in the corresponding atom, there would result a superposition of the bands of the several levels causing an apparent complexity in the appearance of the fine structure. The diminution of the triplet separations in the higher levels would result in a simplification in the structure of the bands involving these levels, and this might account for the less complicated nature of the bands of the 3 A system. On the other hand, if we suppose the levels involving the appearance of the fourth positive bands and Angstrom bands to be singlet levels, then one should expect the structure of these bands to be less complex, which is certainly the case.¹

As stated elsewhere, the observed ionization potential of the molecule was 14.3 volts. The "comet-tail" bands appear at an exciting-voltage of 16.9. Baldet's analysis² indicates that 5281 Å, corresponding to wave-number 18,930 is the 0-0 band of this system. In terms of equivalent energy, this value represents 2.34 volts which yields 16.64 volts as the exciting-potential of this system. Birge³ computes 16.7 volts based on 14.2 volts as the ionizing-potential and 4880 Å as the 0-0 band. Taking this latter band, 4880 Å, as the 0-0 band, with the observed ionization potential, 14.3 volts, the computed critical potential is 16.83 volts.

At 20.0 volts the first negative system appears. Johnson⁴ has made a complete analysis of this system and shows without doubt that the band with head at 2190 Å represents the 0-0 transition. The emission of this band represents a transition of 5.64 volts, which makes the computed critical potential of this system 19.94 volts—in good agreement with the measured value of 20.0 volts. This work confirms the view that these systems have the same final state, which is the normal state of the ionized molecule.

The observed exciting-potential of the Baldet-Johnson bands

¹ Duffendack and Fox, *Nature*, **118**, 12, 1926.

² *Comptes Rendus*, **180**, 272, 1925.

³ *Nature*, **117**, 230, 1926.

⁴ *Proceedings of the Royal Society, Series A*, **108**, 343, 1925.

was 22.9 volts, a value 2.9 volts higher than the exciting-potential of the first negative system. According to the scheme proposed by

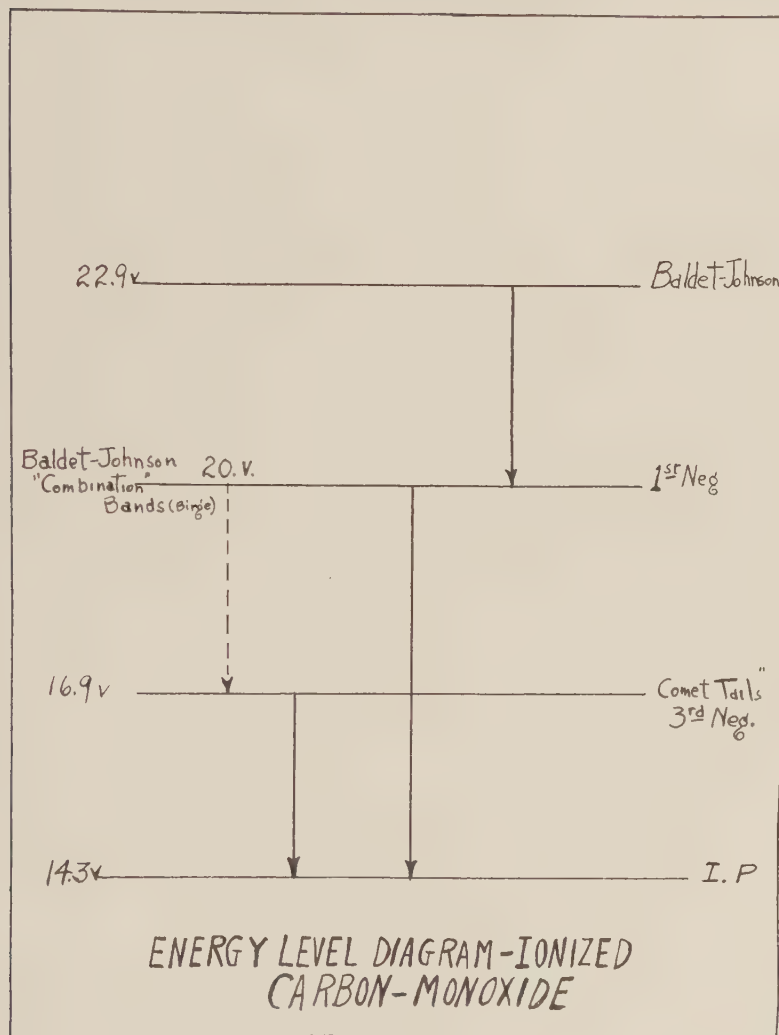


FIG. 4

Birge,¹ this system should be excited at the same critical voltage as the first negative system, based on the observation that the

¹ *Nature*, 117, 230, 1926.

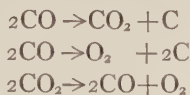
vibrational differences of the initial states of both these systems seem to follow the same progression. As this system contains so few bands, one cannot be certain of the analysis proposed for it; and hence the band corresponding to the $0-0$ transition is unknown. The energy radiated by the strongest band of the system, $3729.8 \text{ \AA}$, corresponds to 3.3 volts. As this is not far from the difference in observed exciting-potentials of this system and the first negative, it suggests that the final states of the Baldet-Johnson bands are the initial states of the first negative bands. However, it has not been possible to work out a satisfactory analysis of the system on this basis.

From physical considerations a combination scheme does not seem likely. It will be remembered that both the "comet-tail" and first negative systems were characterized as low-pressure bands, the "comet-tail" system especially so. On the other hand the Baldet-Johnson bands are produced only at high pressures of the order of a millimeter. They completely disappear at pressures at which the first negative and "comet-tail" systems are best developed. This phenomenon appears best explained by the introduction of new levels, since it seems difficult to reconcile the behavior of the Baldet-Johnson bands with two other systems so different. Recently Ann B. Hepburn (November, 1926, meeting of the American Physical Society) reported the excitation potential of the Baldet-Johnson bands as 23.0 volts in agreement with the results of this investigation. Her measurements of the excitation potentials of the Ångström, first negative and "comet-tail" systems, are also in excellent agreement with the values given above.

PART III. DETERMINATION OF THE ORIGIN OF THE "CARBON-OXIDE" BANDS

Throughout the previous discussion it has been tacitly assumed that all the band systems described belonged to carbon monoxide. Although, it is true, the discharge tube was always filled with pure CO gas at the beginning of each run, there was considerable dissociation, as was evidenced by an increasing thickness of carbon deposit over the electrodes and walls of the tube. Likewise the necessity of frequent renewal of the filament indicated the presence

of oxygen. The possibility therefore of the presence of CO_2 , formed during the passage of the discharge through the tube, did not seem beyond question.



I. Langmuir[†] has definitely shown, however, that CO is not dissociated by thermal action at the surface of a tungsten filament, even when heated to its melting point. The first two reactions cannot occur except through the influence of the discharge.

To test whether any of the observed spectra were due to CO_2 , a discharge tube was connected to a flow apparatus. The filament was, in this case, made of 15 mil platinum wire covered with a heavy coating of calcium, barium, and strontium oxides. This type of filament will give an abundant emission of electrons at a comparatively low temperature and would, therefore, reduce to a minimum the dissociation of CO_2 due to thermal action. Mounted directly in front of this filament was a grid of platinum gauze covering a small window in a sheet of molybdenum which divided the tube into two compartments. The plate of tungsten was mounted about 1 cm from the grid, and the two were then electrically connected. Radiation from the force-free region passed out of the tube through a quartz window.

Carbon dioxide was generated in a vacuum by allowing concentrated sulphuric acid to drop on specially prepared calcium carbonate. The gas thus generated was allowed access to reservoirs which filled to atmospheric pressure. A calibrated stopcock permitted the adjustment of the rate of flow when the pumps were operating so that very uniform pressure conditions could be obtained and maintained indefinitely. Any CO that might have been present was removed by freezing out all the CO_2 in the reservoirs with liquid air and opening the reservoirs to the pumping system through a stopcock. As a matter of fact, however, there was no CO present, as the gauge read zero pressure both before and after this stopcock was opened.

[†] *Chemical Society Journal*, 37, 1162, 1925.

The CO_2 gas entered the discharge tube at the plate end in such a way as to flow against the electron stream, and was then lead out directly above the grid. Thus the radiation examined was that from gas which had not come in contact with the filament, and so was not dissociated by thermal action. After steady pressure conditions had been obtained, the discharge was started and the radiation examined with the spectroscope. Observations were also made with the flow stopped, i.e., in the stagnant gas.

RESULTS

There was a very striking dissimilarity in the color of the discharge in the flowing and stagnant gas. In a previous part of this paper the carbon-monoxide glow was characterized as "sky-blue." The discharge in the CO_2 bore no similarity to this color. It was predominantly purple. The effect of stopping the flow was to change, at once, the color of the discharge from purple to the light blue of carbon monoxide. Likewise in the flowing gas, by increasing the voltage to values of the order of 50 volts, the color of the discharge could be changed from purple over to the blue hue.

Photographs were made with the E2 Hilger spectrograph and with a two-prism glass instrument. The examination of these spectrograms discloses some very interesting information relative to the spectra in the flowing and stagnant gas. With the gas flowing, there was no radiation observed between 2750 Å and the limit of the quartz. From 2750 Å, however, up through the visible, the spectrum of CO_2 appears filled with a band system of very complicated structure. Groups made of multiple heads, shaded decidedly toward the red, follow along in close sequence. So far as is known, this spectrum is not recorded. In the flowing gas at voltages which should have excited the third positive carbon bands very easily, not a trace of these bands appeared. As soon as the flow was stopped however, not only did the third positive bands appear very strongly but also the Ångström bands and first negative bands, while the spectrum due to the flowing gas appeared suppressed in intensity. At the same time the pressure in the system with the stagnant gas increased, as would be expected, from the conversion of CO_2 into CO and O_2 . The foregoing observations lead to the conclusion that the

third positive system of carbon is undoubtedly due to the carbon-monoxide molecule.

In re-examining some of the plates of the CO spectrum in the visible, a peculiar striated appearance of the Ångström bands was noted on some exposures. The explanation seems to be that CO_2 was produced in some cases by the action of the discharge, and the striations are due to the superposition on the Ångström bands of the CO_2 spectrum just described. This may mean that several of the originally reported Ångström bands that were not observed during this investigation really do not belong to this system at all but were due to the excitation of CO_2 formed in the Geissler-tube discharge.

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